# **Demystifying Hazmat Chemistry**

It isn't necessary to be a "propeller head" to understand hazardous materials chemistry. By understanding a few basic concepts, you can build a foundation that will help you safely and confidently handle the majority of hazmat incidents you might encounter.



This course is designed to provide responders with a review of key items in hazmat chemistry (without trying to cram two weeks of chemistry into one afternoon). The information is not new. However, the goal of the course is to provide responders with perhaps some new ways to look at difficult information and to encourage participants to share their ideas with others.

The basics presented here are guidelines only. They are designed to help you manage the initial response phase of a hazmat incident. However, do not rely solely on the information in this handout. It is a very limited tool. It must not be used in place of a proper risk assessment and hazard analysis. Remember that there are exceptions to every rule, that various factors may change the risks, and that if more than one product is involved, it may be difficult to accurately predict the hazards.

(Some of the information in this handout was reprinted with permission from the California Specialized Training Institute.)

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# **Vapor Pressure and Vapor Density**



Approximately 90% of hazmat injuries are due to inhalation. Obviously, this signals a need to protect against exposure to *gases*. However, responders must also be concerned about the *vapors* produced by liquids (and, to some extent, the vapors produced by solids). To determine whether vapors can "get to us," we need to look at vapor pressure.

*Vapor pressure* is the force exerted by the vapors of a product against the atmosphere or the sides of a container. If a liquid has a vapor pressure less than 10 mmHg (millimeters of mercury), the vapors won't travel much beyond the surface of the liquid. However, above 10 mmHg, the vapors will begin to rise into the air. How far and how fast they travel depends largely on vapor pressure. The chart below shows the vapor pressures of several products for comparison.

The Vapor Pressures of Various Products

Material	Vapor Pressure
Sulfuric Acid	0.001 mmHg
Turpentine	4 mmHg
Water	25 mmHg
Isopropyl Alcohol	33 mmHg
Ethyl Alcohol	44 mmHg
Hydrogen Cyanide	630 mmHg
Hydrogen Fluoride	783 mmHg
Chlorine	6.8 atm (roughly 5168 mmHg)
Ammonia	8.5 atm (roughly 6460 mmHg)

Source: NIOSH Pocket Guide

Vapor pressure is normally measured in millimeters of mercury (mmHg) at 68°F at sea level. (If measured at another temperature, that temperature should be identified.) If the vapor pressure equals 760 mmHg at sea level, the product is a gas in its normal state. The closer the vapor pressure is to 760 mmHg, the more vapors a liquid produces and the more you need to protect yourself against those vapors. (Vapor pressure may also be reported in pounds per square inch or atmospheres. A vapor pressure of 760 mmHg is equivalent to 14.7 psi or 1 atmosphere.)

Vapor pressure is temperature-dependent. The greater the temperature, the higher the vapor pressure. The following page contains a chart that shows the vapor pressure of water at various temperatures.

780 720 660 600 540 Vapor Pressure (mmHg) 480 420 360 300 240 180 120 60 100°C 25°C 50°C 75°C 122°F 167°F 32°F 77°F 212°F

The Vapor Pressure of Water at Various Temperatures

Source: Hazardous Materials by Warren E. Isman and Gene P. Carlson

Temperature

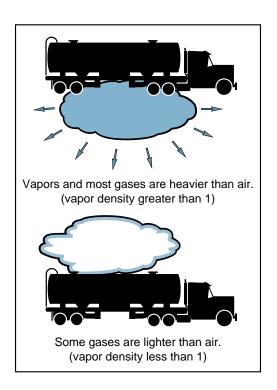
20°C

Vapor density is different from vapor pressure. *Vapor density* is the relative weight of liquid vapors or a gas compared with a like volume of air. Air has a density of 1. Vapors or gases with vapor densities greater than 1 (>1) are heavier than air. Gases with vapor densities less than 1 (<1) are lighter than air.

It is helpful to remember that *all* vapors are heavier than air. Most gases are heavier than air too. Only a handful are lighter, and some of those are actually pretty close to the weight of air.

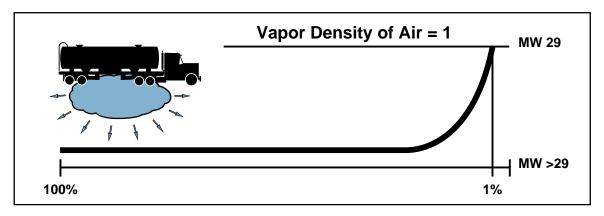
Gases That Are Lighter Than Air

Gas	Vapor Density
Acetylene	0.91
Ammonia	0.60
Carbon Monoxide	0.97
Ethylene	0.967
Helium	0.138
Hydrogen	0.07
Methane	0.553
Natural Gas	0.55
Nitrogen	0.969



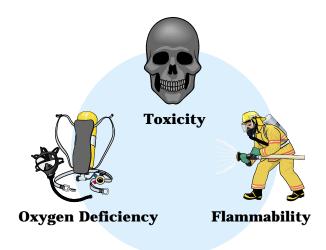
Just because the vapor density is heavier or lighter than air does not mean that the vapor or gas will be found only at one level. Concentration also has a small impact on where a vapor or gas will be found. For example, although gasoline vapors are almost four times heavier than air, if the concentration of vapors is low (close to 1%), the vapors will mix more evenly with air; they won't hug the ground as much as they would in higher concentrations.

# As Concentration Approaches 1%, Vapors Will Mix More Evenly with Air



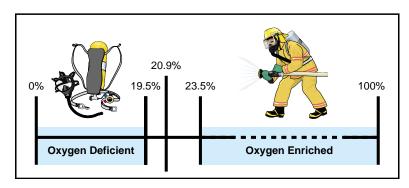
# **Comparing Three Primary Threats**

We generally evaluate hazmat incidents in terms of three threats: oxygen deficiency, toxicity, and flammability. These three threats impact some of the decisions we have to make, for example, what personal protective equipment to wear or what community protective actions to implement.



#### **Oxygen Deficiency**

The normal atmosphere is comprised of roughly 78% nitrogen, 20.9% oxygen, and 1.1% argon and other gases. Although 20.9% oxygen is considered normal, we don't hit the "threat zones" until we drop below 19.5% or rise above 23.5%.

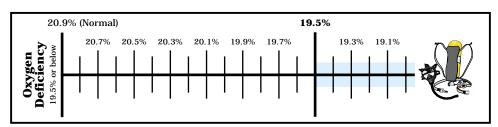


The Limits of an Acceptable Oxygen Concentration

If the oxygen level is above 23.5%, the atmosphere is considered to be potentially explosive. An oxygenenriched atmosphere will cause any flammable or combustible material to ignite more readily and burn more fiercely.

For the purposes of this discussion, however, we want to focus on oxygen-deficient atmospheres. An oxygen concentration of 19.5% is considered by OSHA and NIOSH to be the minimum safe level. Below that, responders must wear self-contained breathing apparatus (SCBA) or a supplied air respirator (SAR). Airpurifying respirators (APR) are not acceptable under these conditions, even if they are capable of filtering contaminants present in the atmosphere, because they do not provide responders with a source of oxygen.

A simple hazard ladder such as the one below makes it easy to determine if you are in the threat zone for oxygen deficiency (depicted by the shaded section).



# An Oxygen Deficiency Hazard Ladder

Keep in mind that a concentration of 19.5% oxygen is not an immediate threat to life. It still provides a margin of error. The following chart shows the effects of oxygen deficiency on one's mental and physical abilities.

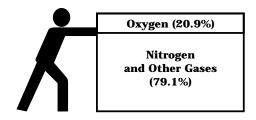
Oxygen Level	Effects
20.9%	(Normal concentration)
19.5%	(Minimum safe level per OSHA and NIOSH)
16%	Disorientation, impaired judgment, impaired breathing
14%	Faulty judgment, rapid fatigue
8%	Mental failure, fainting
6%	Difficulty breathing, death within minutes

The Effects of Oxygen Deficiency

However, it's also important to note that any displacement in the oxygen concentration is a warning signal that there may be a contaminant present in the atmosphere, assuming your meter is working properly. Further monitoring is required.

Since oxygen comprises roughly one fifth (1/5) of the normal atmosphere, a 1% oxygen displacement means there is roughly a 5% concentration (50,000 ppm) of a contaminant gas or vapor. In other words, although your meter is showing a 1% displacement, that contaminant gas or vapor is really displacing one part oxygen and four parts everything else. (The illustration on the right shows the relation between percent by volume and parts per million [ppm] and parts per billion [ppb].)

Atmospheric Displacement (One Part Oxygen and Four Parts Everything Else)



The Relation Between Percent (%) by Volume and ppm and ppb

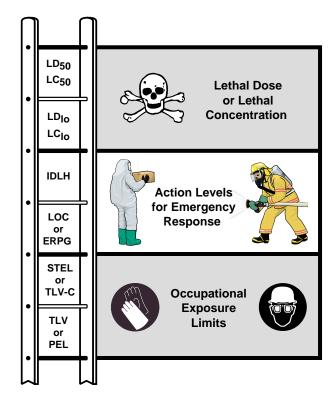
% by volume	ppm	ppb
0.1%	1,0000	1,000,000
1%	10,000	10,000,000
10%	100,000	100,000,000

#### **Toxicity**

There are many terms and associated abbreviations used to describe exposure limits and toxicity values. This alphabet soup of terms and abbreviations can be very confusing to someone new to hazardous materials. Putting these values on a "hazard ladder" that shows relation between them can help responders understand toxicity a little better.

The illustration below divides the most common exposure limits and toxicity values into three groups for easy reference. The illustration is obviously not to scale, but it does provide a quick visual representation of how these values stack up against one another.

At the top of the ladder are the lethal doses or concentrations. These are the exposures required to produce a lethal effect in a given percentage of a test population. These numbers are of limited value to us because there are no acceptable losses in emergency response. We need to implement protective measures long before reaching these levels.



Exposure Limits and Toxicity Values Compared

At the bottom of the ladder are the workplace exposure levels. The exposure limits are based on workers without protective clothing, other than perhaps goggles, gloves, and aprons to protect against splashing or other inadvertent contact. These values represent no unusual risks to emergency responders, but may become significant in a protracted incident if personnel are not wearing respiratory protection.

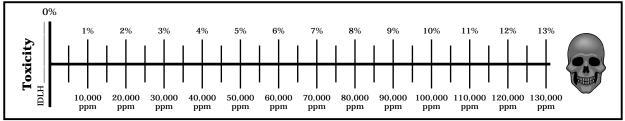
The values we use most often in emergency response are IDLH and LOC. *IDLH* (*Immediately Dangerous to Life and Health*) means an atmosphere that poses an immediate threat to life, would cause irreversible adverse health effects, or would impair an individual's ability to escape from a dangerous atmosphere. As a safety margin, IDLH values were based on effects that might occur from a 30-minute exposure, but it was not meant to imply that workers should stay in the environment without proper PPE any longer than necessary. In fact, every effort should be made to exit immediately. IDLH is established by OSHA and NIOSH.

IDLH is often used to distinguish between a rescue and a body recovery operation. If a victim has been exposed to the product at or above an IDLH concentration for more than 30 minutes, the chances of survival drop significantly. However, IDLH is only part of the "risk versus gain" analysis. It is generally not possible to make a positive determination of death from a distance.

*LOC* (*Level of Concern*) is the value used to determine the geographic area of risk in the event of a chemical release. This is generally the point at which evacuation or in-place protection measures are implemented.

Shown below is a hazard ladder to plot toxicity, similar to the one used to plot oxygen deficiency. Later you'll see how the two can be used together to help assess risk.

# A Toxicity Hazard Ladder



Unfortunately, there may be times when you can't find IDLH or LOC in your reference books, particularly books geared toward workplace exposures. For those occasions, you can estimate IDLH or LOC if you know the TLV-TWA. LOC is generally defined as 10% of the IDLH or 3 times the TLV-TWA; thus IDLH is 10 times the LOC or 30 times the TLV-TWA. Remember, however, that these are approximations only.

TLV-TWA (Threshold Limit Value—Time Weighted Average) is the upper limit of a toxic material to which an average person in average health may be exposed repeatedly on a day-to-day basis (40 hours per week, 8 hours per day) with no adverse health effects. It is specifically geared towards airborne exposures, but may include a "skin" notation if the particular material is readily absorbed through the skin. Limited excursions above the TLV are permitted when the average exposure over an 8-hour day does not exceed the TLV-TWA.

Other values shown on the illustration on the previous page are PEL, STEL, and TLV-C. *PEL (Permissible Exposure Limit)* is also defined as the maximum permitted exposure for an 8-hour time-weighted average. Often it is the same number as the TLV. However, PEL is a legal limit established by OSHA, whereas TLV-TWA is a recommendation set by the American Conference of Governmental Industrial Hygienists (ACGIH). *STEL (Short-Term Exposure Limit)* is the maximum concentration that a worker may be exposed to for short durations (limited to a maximum of 15 minutes per exposure). Exposures above the STEL should be at least 60 minutes apart and not repeated more than 4 times per day. *TLV-C (Threshold Limit Value–Ceiling)* is similar to STEL. However, exposure to this concentration must not be exceeded for any reason. Exposures at or below the TLV-C are allowable provided that the average exposure throughout the work week does not exceed the TLV-TWA.

#### **Flammability**

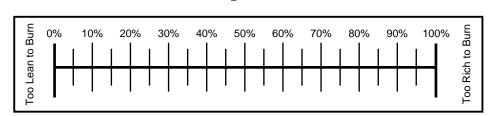
When plotting the flammability risk on a hazard ladder, we generally look at the concentration of a gas or vapor in air, just as we do when plotting toxicity. The most important value is the *Lower Explosive Limit* (*LEL*). Below the LEL, vapors are too lean to burn. At the other end of the scale is the *Upper Explosive Limit* (*UEL*). Above this concentration, vapors are too rich to burn. However, from the LEL to the UEL, ignition is possible. This is known as the *flammable range*.

# 10% LEL Unsafe (Threat Zone) Too Lean to Burn Too Rich to Burn The Flammable Range

Flammable Range

Only atmospheres that are well below the LEL are safe to enter. The cutoff we often use is 10% of the LEL. That gives us a wide margin of error to account for variations in concentration in different areas, malfunctions in our monitoring equipment, and a host of other factors that may compromise our safety. Although the vapors are too rich to burn above the UEL, you should not consider that to be a safe atmosphere since the vapor concentration may drop to within the flammable range during your emergency response operations.

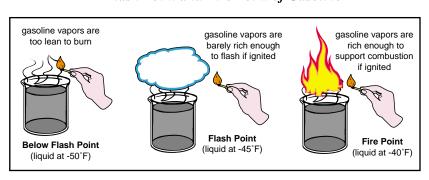
You can plot flammable range on a hazard ladder also. This gives you a clear visual representation of the flammability risk. The wider the flammable range, the greater the risk. Conversely, products with a narrow flammable range present less of a risk.



Plotting LEL and UEL

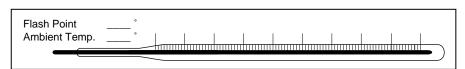
Flammable range is not the only concern, however. We also need to consider *flash point* when looking at flammable liquids. Flash point is generally considered to be the most important temperature in assessing the hazards of flammable and combustible liquids. Flash point is the minimum temperature at which a liquid produces enough vapor to form an ignitable mixture in air. The flame does not continue to burn at the flash point when the source of ignition is removed; it only flashes. The lower the flash point, the greater the hazard.

Closely related to flash point is *fire point*, the temperature at which enough vapors are now given off to support continuous burning even after the source of ignition has been removed. Because the fire point is generally just a few degrees higher than the flash point, we tend not to worry about it in emergency response. Using the flash point gives us a greater margin of safety.



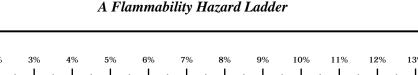
Flash Point and Fire Point of Gasoline

If you want a visual representation of flash point, you can plot it on a ladder that shows its relation to ambient temperature.



#### Plotting Flash Point and Ambient Temperature

Shown below is another hazard ladder for flammability. We'll need this one shortly to compare flammability, toxicity, and oxygen deficiency on an equal basis. Notice that this ladder is designed to show LEL but not UEL. That's because we really need to know only the LEL to evaluate risk.



#### 0% lammability 13% 10,000 20,000 30.000 40,000 50,000 60,000 70,000 80,000 90,000 100,000 110,000 120,000 130,000 ppm ppm

There are two other properties worth mentioning, ignition temperature and boiling point, although they are less important that flammable range and flash point. The *ignition (autoignition) temperature* of a substance is the minimum temperature required to cause self-sustained combustion (independent of an ignition source). The illustration below shows gasoline vapors (with an ignition temperature of 853°F) being ignited by a lit cigarette. The burning end of a lit cigarette generates roughly 975°F.



Ignition Temp of Gasoline 853°F

**Ignition Temperature** 

Once again, however, the ignition temperature is *independent of an ignition source*. A good example of autoignition is in a fire situation where convection carries hot air and gases to other parts of a building. When the atmosphere becomes hot enough to the point where these gases reach their ignition temperatures, they will ignite automatically without the introduction of any other ignition source. Autoignition temperature can be somewhat difficult to measure and should be considered an approximation.

*Boiling point* is the temperature at which the vapor pressure equals the atmospheric pressure at the surface of the liquid. It is the point of maximum vapor production. The lower the boiling point, the greater the hazard potential because it takes less heat to get that liquid to the point of maximum vapor production.

**Boiling Point** 



#### **Comparing the Three Threats**

Oxygen deficiency, toxicity, and flammability can be plotted on parallel ladders. We already know that cutoff for oxygen deficiency is 19.5%. Anything below 19.5% is considered to be within the threat zone. Therefore, we can easily plot that on a hazard ladder.

We generally use IDLH when looking at the toxicity threat. Therefore, you can write in the IDLH value at the left side of that ladder, then plot the concentration according to either percentage or parts per million. A concentration of 1% is equal to 10,000 ppm, so regardless of which measurement you use, you can plot it accurately. Anything to the right of where you draw your line is considered to be within the threat zone.

You can do the same with flammability. Although you will plot only LEL, you should identify the flash point and ignition temperature too because these temperatures will help you assess the risk.

#### 20.9% 19.5% 20.1% 19.9% 19.3% 19.1% Deficiency 19.5% or below 0xygen 0% 3% 4% 5% 6% 7% 8% 9% 1% Toxicity IDLH 80,000 10,000 90,000 20.000 30,000 40,000 50,000 60,000 70,000 ppm ppm ppm ppm ppm ppm ppm ppm ppm 0% Flammability 1% 2% 3% 4% 5% 6% **7**% 8% 9% Flash Point \_\_\_\_\_Ignition Temp\_\_ 10,000 90,000 20.000 30,000 40.000 50.000 60.000 70.000 80 000 ppm ppm ppm ppm ppm ppm ppm ppm ppm

#### Parallel Hazard Ladders

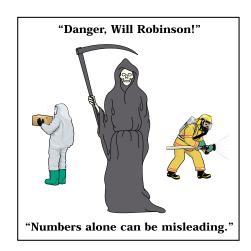
If you have a reading of 19.5% oxygen—the minimum safe level per OSHA and NIOSH—you can have slightly less than 6.7% (or 67,000 ppm) of a contaminant gas or vapor present in the atmosphere. (Remember: Oxygen comprises 20.9% of the normal atmosphere. If you divide the oxygen displacement—in this case, 1.4%—by .209, the result is 6.699.) If you look at the three ladders on this page, you will see that they line up pretty closely.

By plotting all three threats on parallel ladders, you can easily identify which one you will encounter first. For example, if you had a product with an IDLH of 2% (or 20,000 ppm) and an LEL of 8.5% (or 85,000), it becomes clear that you will encounter a toxic atmosphere before you encounter an oxygen-deficient atmosphere or a flammable atmosphere. (Of course, you could tell this just by looking at the numbers. The illustration simply makes it easier to visualize.) However, let's take a look at another example, one where the numbers are closer and where numbers alone can be misleading. The following illustration shows gasoline plotted on three parallel hazard ladders. As you can plainly see, the IDLH of gasoline (estimated to be 9000 ppm) is lower than the LEL (1.4% or 14,000 ppm).

#### 19.5% 20.9% Gasoline 5% IDLH 20,000 ppm 40,000 ppm 50,000 ppm 70,000 ppm 10.000 30.000 60.000 80.000 90.000 3% 10,000 20,000 30,000 40,000 50,000 60,000 70,000 80,000 90,000

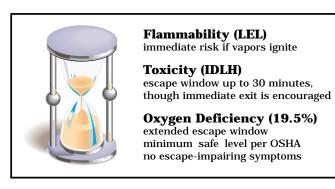
#### Gasoline Plotted on Three Parallel Ladders

Numbers do not always tell the whole story, however. Going strictly by the numbers, one might think that you will encounter a toxic atmosphere before you encounter a flammable atmosphere. But you need to look at the big picture to accurately assess this threat. You need to look at the numbers in relation to your incident objectives and operations. And you may find you need to look at different exposure values based on those operations and how much time they take.



Again, time is an important factor in assessing risk. The illustration below puts the three primary threats in perspective with regard to time. If you're in an LEL atmosphere when flammable vapors find an ignition source, you are in immediate danger; there's no escape window. (Of course, if you have eliminated all ignition sources, you don't have to worry about this.) IDLH used to be defined as having a 30-minute escape window because the IDLH values were based on effects that might occur from a 30-minute exposure. Unfortunately, however, some people interpreted that as permission to stay in an IDLH environment without proper PPE so long as they did not exceed the 30-minute time frame. But that was never the intent of IDLH, so the official definition was changed to omit the 30-minute reference. Every effort should be made to exit the atmosphere right away, but the danger isn't as immediate as it is in an LEL atmosphere. Finally, oxygen deficiency has an extended escape window because the 19.5% limit provides a comfortable safety margin.

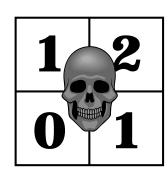
Three Primary Treats in Perspective with Regard to Time

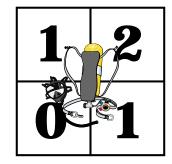


Other factors often impact the degree of risk, so you may need additional tools to adequately assess the situation. For example, flammability is no longer an immediate problem if you can completely eliminate ignition sources, regardless of the LEL or flash point. The three matrices below can be used as a foundation to assess the degree of risk for flammability, toxicity, and oxygen deficiency. The matrices are flexible enough to be modified as needed, based on whatever factors you need to evaluate. We'll go through a scenario on the following pages to show you how this tool works.

Simple Matrices That Can Be Used As a Foundation for Assessing Risk





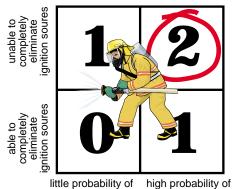


Let's take the scenario of an overturned MC-306 with gasoline running down the street and into the storm drains. You need to assume that there is a high probability of having an LEL concentration somewhere in the area. Unless the ambient temperature is below -45°F, the gasoline will be above its flash point. And chances are that you will be unable to completely eliminate ignition sources in the area. Flammability is an immediate concern. A high probability of reaching LEL and flash point combined with the inability to completely eliminate ignition sources gives us a score of 2 (right).

In a different scenario, we might get a different rating. For example, if we can completely eliminate ignition sources but still have an LEL atmosphere, we would earn a score of 1 on the matrix. Why not 0? Because our efforts to eliminate all ignition sources may not be foolproof. The bozo with a cigarette who sneaks past a control line can quickly endanger everyone.

#### A Flammability Matrix

# Flammability (LEL)



reaching LEL and/or flash point

nigh probability of reaching LEL and flash point

IDLH values, once again, were based on 30-minute exposures. So while you may reach an IDLH concentration of gasoline before you reach a flammable concentration of gasoline, the risk to people in the area will not be immediate. (A person can stand in a garage filled with gasoline vapors at 1.4% and not be in immediate danger from breathing the vapors. However, if the gasoline ignites, there's no 30-minute escape window.) Consider, too, that people in the area are likely to detect the odor of gasoline, recognize the *fire* danger, and either evacuate on their own or call 911 and receive evacuation instructions before reaching a point where they would be in danger from toxicity. So we can give gasoline a 1 on the toxicity matrix (below left) as we assess the need for public protection.

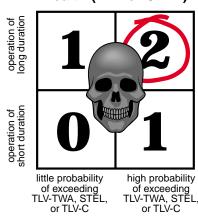
However, as we said earlier, you may need to look at other exposure values depending on the incident objectives. For example, let's say that the gasoline has spilled into an active creek. We've assigned personnel to build an underflow dam downstream, and we know it's going to take several hours to complete the job. The vapor concentration is safely below the LEL, but higher than the TLV-TWA, STEL, or TLV-C. In this case, we would have to assign gasoline a 2 on the health effects scale (below right) and put more emphasis on protecting our personnel from adverse health effects.

#### A Toxicity Matrix

# Toxicity (IDLH) and self-evacuate and self-evac

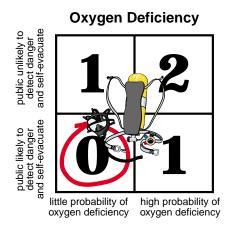
#### A Health Effects Matrix

#### Health (TLV or STEL)



Let's again look at the issue of public protection from our gasoline spill. The probability of reaching an oxygen-deficient atmosphere is low. And while the public cannot detect oxygen deficiency, people will recognize the fire danger once they detect the odor of gasoline. They will either self-evacuate or be directed to evacuate based on the fire danger long before oxygen deficiency is a concern. Our gasoline spill rates a 0 on the oxygen deficiency scale. Remember, too, that oxygen deficiency has an extended escape window. The 19.5% level established by OSHA and NIOSH provides a big margin of safety.

# An Oxygen Deficiency Matrix



Keep in mind that the hazard ladders and matrices presented in this handout are simply tools to help you look at the big picture. But none of them represents the big picture by themselves. The matrices on these last two pages were useful in our gasoline scenario because the IDLH and LEL values were so close. With a different chemical, you might have a situation in which the product was so toxic that by the time you reached an LEL atmosphere, you were also in a lethal concentration as opposed to an IDLH environment.

#### The Classification of Matter

Matter is anything that occupies space and has mass. It is often classified as shown below.

## Matter Pure Substance Mixture Element\* Compound Metal Nonmetal Salt\* Nonsalt Metalloid Organic Inorganic Topics addressed Hydrocarbon\* Hydrocarbon in this handout. **Derivative\***

The Classification of Matter

This handout provides "cheat sheets" for four of the classifications (elements, salts, hydrocarbons, and hydrocarbon derivatives) because it is possible to make some generalizations about them. The hazards identified herein are listed because either they are true for the majority of chemicals within the given category or they represent the hazards associated with some of the worst chemicals within the group.

At one extreme, it can be dangerous to assume that these generalizations apply to all chemicals within a given category. For example, most aromatic hydrocarbons are stable. Styrene, however, contains a double bond between carbon atoms outside the resonant structure. It is less stable than other aromatic hydrocarbons because of this double bond.

Conversely, you can easily blow an incident out of proportion by failing to recognize that not all products in a given category are equally hazardous. For example, sodium chloride (NaCl) is a binary salt, but if you failed to recognize that it is ordinary table salt, you might wrongly assume that it was very dangerous. There are many other such examples, most of which have names you might not recognize.

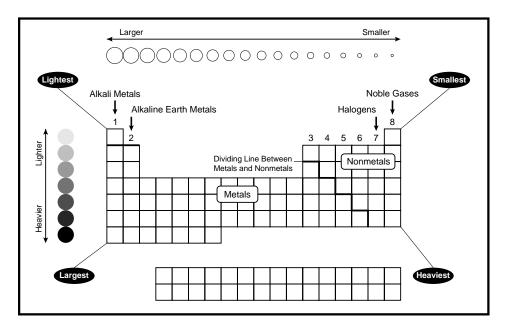
Chemicals don't always fit neatly into specific categories. For example, while salts are generally described as containing a metal bonded to a nonmetal, some contain no metal at all. The ammonium ion  $(NH_4)$  acts like a metal, so ammonium nitrate  $(NH_4NO_3)$  is considered an oxysalt even though there is no metal in the compound.

This handout won't identify the multitude of exceptions that exist. It won't help you recognize when chemicals have multiple names. Nor does it show how hazards or risks can change based on form (solid, liquid, gas), concentration, external factors (such as temperature), or the presence of other chemicals. However, if you understand the limitations and use it accordingly, this handout can be a valuable tool.

#### The Periodic Table of Elements

Elements on the periodic table are arranged according to their atomic structure. The illustration below is that of a blank periodic table designed to show how an element's position on the periodic table will give you some basic information about its characteristics. (A complete periodic table is shown on the following page.)

Metals are located on the left side of the periodic table; nonmetals, on the right. (Notice the dividing line between metals and nonmetals.) Hydrogen, in the upper left-hand corner is also a nonmetal.

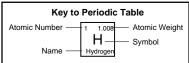


Trends on the Periodic Table

The elements become heavier as you go lower on the table, which is significant with respect to vapor density, specific gravity, and other related properties. Elements toward the left side of the periodic table are larger, whereas those toward the right side are smaller and more compact.

The periodic table on the following page shows each element by name, symbol, and atomic number. (The atomic weight was rounded to three decimal points where the number was less than 100. Atomic weights over 100 were rounded to two decimal points.) The symbols consist of either a single capital letter (for example, H for hydrogen) or a capital letter followed by a lowercase letter (for example, He for helium.)

Key to the Periodic Table on the Following Page



#### Alkali Metals Noble Gases Η He 10.8 B 12.0° O 15. Li Be Ν Ne Si CI Na Mg ΑI S Ar K Sc Со Ga Ca Τi Cr Mn Fe Ni Cu Zn Ge As Br Se Kr Ag Rb Sr Zr Nb Мо Tc Ru Rh Pd Cd In Sn Sb Te Xe Cs Ba La Hf Ta W Re Os lr Au Hg ΤI Pb Rn Fr Unq Ra Ac Unp Unh Uns Uno Une Pm Ce Pr Sm Dy Yb Nd Eu Gd Tb Ηо Er Tm Lu Čm Th Pa U Np Pu Bk Cf Es Am Fm

#### The Periodic Table of Elements

Elements are grouped vertically in families based on their chemical behaviors. All members of the same family have similar chemical characteristics, though each will also have its own unique properties. The four families identified below are significant because the similarities between each member of the family are greater than they are within other families.

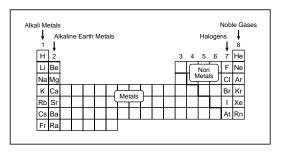
**Group I - The alkali metals** are lithium, sodium, potassium, rubidium, cesium, and francium. These elements are flammable and highly reactive. When in contact with water, they produce flammable hydrogen gas, a strong caustic runoff, and excessive heat.

**Group II - The alkaline earths** are beryllium, magnesium, calcium, strontium, barium, and radium. These alkaline earths (Group II) are flammable and water-reactive, though less so than the alkali metals (Group I).

**Group VII - The halogens** are fluorine, chlorine, bromine, iodine, and astatine. These elements are highly reactive, toxic, and powerful oxidizers. They are nonflammable.

**Group VIII - The noble gases** are helium, neon, argon, krypton, xenon, and radon. These gases are inert, nonreactive simple asphyxiants that are often stored and transported as cryogenic liquids.

#### Four Significant Families



Most elements exist as solids in their natural states. The elements that exist as gases are hydrogen, nitrogen, oxygen, chlorine, fluorine, and the noble gases (helium, neon, argon, krypton, xenon, and radon). Periodic tables generally identify bromine, cesium, francium, and mercury as liquids. However, some elements are borderline and may exist in different forms, depending on ambient temperature.

# Hydrocarbons

Hydrocarbons can often be identified by name. Most use specific prefixes to indicate the number of carbon atoms in the formula and use specific endings to identify the type of hydrocarbon. However, there are exceptions. For example, despite the *-ene* ending, acetylene is an alkyne. (Acetylene is also known as *ethyne*.)

The aromatic hydrocarbons use different prefixes than do the other hydrocarbons. Looking at the smallest chart below, you can also see that there are exceptions to some of the formulas too. For example, the formula for styrene ( $C_8H_8$ ) does not follow the pattern for the other aromatics.

# Hydrocarbon Identification

Naming Hydrocarbons				
# Carbons	Prefix(es)	Examples		
1	Meth- (Form-)	Methane, Formaldehyde		
2	Eth- (Acet-) (Vinyl-)	Ethane, Acetylene, Vinyl Chloride		
3	Prop- (Allyl-) (Acryl-)	Propane, Acrylonitrile		
4	But-	Butane		
5	Pent- (Amyl-)	Pentane, Amyl Acetate		
6	Hex- (Ben-) (Phen-)	Hexane, Benzene, Phenol		
7	Hept-	Heptane		
8	Oct-	Octane		
9	Non-	Nonane		
10	Dec-	Decane		

Types of Hydrocarbons					
Type Ending Bond Formula					
Alkane	-ane	single	C <sub>n</sub> H <sub>2n+2</sub>		
Alkene	-ene	double (pi)	$C_nH_{2n}$		
Alkyne	-yne	triple	C <sub>n</sub> H <sub>2n-2</sub>		
Aromatic	-ene	resonant (ring)	$C_nH_{2n-6} \ (n \ge 6)$		

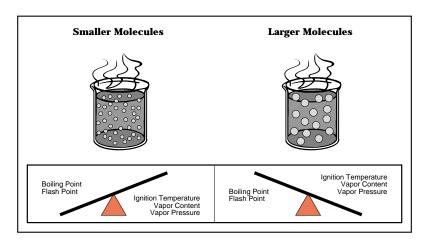
The Aromatics			
Name Formula			
Benzene	C <sub>6</sub> H <sub>6</sub>		
Toluene	C <sub>7</sub> H <sub>8</sub>		
Xylene	C <sub>8</sub> H <sub>10</sub>		
Styrene	C <sub>8</sub> H <sub>8</sub>		
Cumene	C <sub>9</sub> H <sub>12</sub>		

All hydrocarbons have common characteristics. All burn, though some are flammable and others are combustible, depending on flash point. All have some degree of toxicity. All are floaters. Differences between the types of hydrocarbons are based primarily on the types of bonds between carbon atoms. Most alkanes (single bonds) and aromatics (resonant bonds) are relatively stable, the major exception being styrene, which is less stable than other aromatics because of a double bond between carbon atoms outside the resonant structure. Alkenes are less stable because of their double bonds. Alkynes are highly unstable because of their triple bonds.

# Hydrocarbon Characteristics

Common Characteristics of Hydrocarbons			
Type Bond Common Characteristics			
Alkane	single	Stable.	
Alkene	double (pi)	Less stable. Could polymerize.	
Alkyne	triple	Highly unstable. Could explode.	
Aromatic	resonant (ring)	Stable. Toxic. Some carcinogenic. Burn with sooty smoke.	

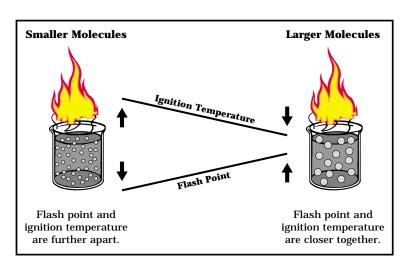
We've raised the topic of molecular size both on the previous page and on page 19, where we first introduced the periodic table. Molecular size has a direct effect on physical and chemical properties. Many of these properties are directly or indirectly proportional to one another, as you can see below.



The Effect of Molecular Size

Flash point and ignition temperature are inversely proportional. Small molecules produce *more* vapor. Therefore, flash point is *lower*; it takes *less heat* to raise the temperature of the liquid to the point where it produces sufficient vapors to form an ignitable mixture in air. However, it takes *more heat energy* to ignite those vapors because they contain less hydrogen (fuel) than do the vapors produced by a larger molecule. The flash point and ignition temperature are further apart in relation to each other.

Larger molecules, by comparison, produce *less* vapor. The flash point is *higher*; it takes *more heat* to raise the temperature of the liquid to the point where it produces sufficient vapor to form an ignitable mixture in air. However, when the ignitable mixture is produced, the vapors are closer to their ignition temperature. It takes *less heat energy* to cause ignition. The flash point and ignition temperature are closer together in relation to each other. Because these larger molecules contain more hydrogen (fuel), they will also output more heat than do smaller molecules.



The Relation Between Flash Point and Ignition Temperature

# **Hydrocarbon Radicals and Hydrocarbon Derivatives**

Hydrocarbon derivatives are comprised of a hydrocarbon radical attached to a functional group. A *hydrocarbon radical* is a hydrocarbon compound in which one or more hydrogen atoms have been removed.

The 1	Making	of a	Hydrod	carbon	Radical
-------	--------	------	--------	--------	---------

Original Hy	drocarbon	Hydrocarbon Radical	
Methane	CH <sub>4</sub>	Methyl	CH <sub>3</sub> _
		Form-	H(C)≡
Ethane	C <sub>2</sub> H <sub>6</sub>	Ethyl	C <sub>2</sub> H <sub>5</sub> _
		Acet-	CH <sub>3</sub> (C) <sub>≡</sub>
Ethene	C <sub>2</sub> H <sub>4</sub>	Vinyl	C <sub>2</sub> H <sub>3</sub> _
Propane	C <sub>3</sub> H <sub>8</sub>	Propyl	C <sub>3</sub> H <sub>7</sub> _
Propene	C <sub>3</sub> H <sub>6</sub>	Allyl, Acryl	C <sub>2</sub> H <sub>3</sub> (C) <sub>≡</sub>
Butane	C <sub>4</sub> H <sub>10</sub>	Butyl	C <sub>4</sub> H <sub>9</sub> _
Benzene	C <sub>6</sub> H <sub>6</sub>	Phenyl	C <sub>6</sub> H <sub>5</sub> _

Hydrocarbon radicals do not exist by themselves because the compounds would not be electrically balanced. The missing hydrogen atoms must be replaced by something else. When a hydrocarbon radical is combined with another element or compound, it forms a *hydrocarbon derivative*. The chart below provides a simple overview of the hydrocarbon derivatives. A more detailed summary is provided on the following page.

The hydrocarbon derivatives can be divided into groups based on the elements that comprise them. Part 1 hydrocarbon derivatives contain only carbon, hydrogen, and oxygen. The group is further divided by general structure. The carbonyls all have a double bond between the carbon and oxygen within their structures; the others do not. Part 2 hydrocarbon derivatives may contain carbon, hydrogen, or oxygen, but they also contain other elements.

#### Grouping of Hydrocarbon Derivatives

Part 1 Hydrocarbon Derivatives (contain only carbon, hydrogen, and oxygen)		Part 2 Hydrocarbon Derivatives (contain other elements)	
Carbonyls Ketones Aldehydes Organic Acids Esters  Carbonyls Alcohols Alcohols Glycols Glycerols Ethers Organic Peroxides		Contain Nitrogen Nitros Amines Nitriles Carbamates Amides	Contain Other Thiols Alkyl Halides Organophosphates Hi-Tech Compounds

Key to Chemical Symbols on Next Page					
As = Arsenic	N = Nitrogen				
B = Boron	O = Oxygen				
Be = Beryllium	P = Phosphorus				
Br = Bromine	S = Sulfur				
C = Carbon Si = Silicon					
CI = Chlorine Sn = Tin					
F = Fluorine Ti = Titanium					
H = Hydrogen X = Alkyl Halide					
I = lodine					
R = Hydrocarbon Radical					

The chart below shows the structure of each hydrocarbon derivative, as well as the key to recognizing each in a chemical formula. The hazards listed are common for some of the worst chemicals in each category.

# Hydrocarbon Derivatives

Part 1 Hydrocarbon Derivatives				Part 2 Hydrocarbon Derivatives			
Туре	Structure	Key to Formula	Common Hazards	Type Structure Key to Formula Common			Common Hazards
Ketones	O R-C-R	со	Toxic. Flammable. Narcotic.	Nitros R-N O		NO <sub>2</sub>	Highly flammable. Explosive. Toxic.
Aldehydes	O R-Č-H	СНО	Toxic. Flammable. Wide flammable range. Over time, may form explosive peroxides.	Amines	Amines R-N <h(r)< td=""><td>Toxic. Flammable. Corrosive.</td></h(r)<>		Toxic. Flammable. Corrosive.
Organic Acids	О R-С-О-Н	соон	Toxic. Corrosive. Combustible.	Nitriles (Cyanides)	P-C-EN		Toxic. Flammable. Some polymerizable.
Esters	O R-Č-O-R	COO or CO <sub>2</sub>	Toxic. Flammable. May form polymers (if unsaturated).	Carbamates	(R)H \ N-C-O-R	NH <sub>2</sub> COO	Toxic. Combustible.
Alcohols	R-O-H	ОН	Toxic. Flammable. Wide flammable range. Undergo slow oxidation.	Amides O R-C-N\(\frac{H(R)}{H(R)}		CONH <sub>2</sub>	Low to moderate toxicity. Flammable. Some polymerizable.
Glycols	(R-O-H) <sub>2</sub>	(OH) <sub>2</sub>	Toxic. Combustible.	Thiols R-S-H		SH	Flammable. Toxic.
Glycerols	(R-O-H) <sub>3</sub>	(OH) <sub>3</sub>	Toxic. Combustible.	Alkyl Halides R-X		F, Cl, Br, or I	Toxic.
Ethers	R-O-R	0	Very volatile. Flammable. Wide flammable range. Over time, form explosive peroxide crystals.	Organo- phosphates	R-P(	Р	Toxic. May be mixed in flammable liquid.
Organic Peroxides	R-O-O-R	OO or O <sub>2</sub>	Explosive. Extremely unstable. Oxidizer. Temperature-sensitive.	Hi-Tech Compounds	May vary greatly	B, Si, As, Be, Sn, or Ti	May be reactive, pyrophoric, toxic.

#### **Salts**

Most salts are comprised of a metal bonded to a nonmetal. The chart below identifies the types of salts, their composition, how they are named (along with examples), and some of the associated hazards. The generalizations listed below under Common Hazards apply primarily to salts containing alkali metals (Group 1) and alkaline earth metals (Group 2). In general, when salts contain transition metals, toxicity and environmental damage are common concerns; reactivity is usually less of a problem.

Types of Salts and	Common Haz	vards Associated	with Them
Types of Dans and	Common Hus	an us 11ssociuicu	WILL TILCIL

Salt	Composition	Naming	Example	Common Hazards of Some of the Worst Salts in Each Category
Binary Salts	metal + nonmetal (not otherwise listed below)	metal + nonmetal root (ends in "ide")	CaC <sub>2</sub> calcium carbide	Toxic. May be water-reactive. Produce a flammable and/or toxic gas when mixed with water (e.g., calcium carbide produces flammable acetylene gas, aluminum chloride produces nonflammable toxic hydrogen chloride gas). Metal sulfides (metal + sulfur) react with acids to produce toxic hydrogen sulfide gas.
Metal Cyanide	metal + cyanide	metal + "cyanide"	KCN potassium cyanide	Toxic. React with acids to produce toxic hydrogen cyanide gas.
Metal Oxide	metal + oxygen	metal + "oxide"	Na <sub>2</sub> O sodium oxide	Water-reactive. Produce heat and a caustic solution when mixed with water, often igniting nearby combustibles. Metal oxides containing alkali metals (Group I) are extremely destructive to skin and metal. (Despite the name, most metal oxides are not oxidizers and do not offgas when exposed to water.)
Metal Hydroxide	metal + hydroxide	metal + "hydroxide" (or alkali, caustic, or base)	NaOH sodium hydroxide	Very caustic and destructive. Water-reactive. Will react with moisture on the skin. Extremely destructive to human skin and other body tissues.
Metal Peroxide	metal (Group I or II) + peroxide	metal + "peroxide"	Na <sub>2</sub> O <sub>2</sub> sodium peroxide	Very strong oxidizers; react with reducing agents (fuel). Water-reactive; can react violently. Produce a caustic solution, heat, and oxygen gas when mixed with water.
Metal Oxysalts	metal + element + oxygen	metal + oxyradical (ends in "ate" or "ite") (may include prefix "per" or "hypo")	NaNO <sub>3</sub> sodium nitrate	Very strong oxidizers; react with reducing agents (fuel). The ending "ate," particularly when preceded by the prefix "per" (for example, perchlorate), signifies a high oxygen content. Oxysalts formed with halogens (e.g., chlorates or bromates) or nitrogen (nitrates) are the most hazardous.

If you suspect that you are dealing with a salt but are not yet sure which one or what hazards are associated with it, assume the worst. Assume it is a caustic, toxic, and water-reactive oxidizer. Don't touch or inhale the product. Use respiratory and skin protection. Keep the product dry. Keep it away from acids and combustibles.

Remember, the common hazards listed above represent the hazards associated with some of the worst salts in each category. The information does *not* apply universally to *all* salts within each category.

# **Simplified Field ID for Unknown Liquids**

Developed by Kevin Smith, Deputy Fire Marshal - Hazardous Materials Chino Valley Independent Fire District

You can often tell a lot about the type of product you are dealing with and the hazards associated with it through simple observation and by doing a few easy tests. The following information is a brief guide. It is not a substitute for more thorough testing or further research using available reference materials. However, it can give you a basis of information from which to make initial response decisions.

#### **Step 1 - Estimate Vapor Pressure**

- 1. Set up two watch glasses.
- 2. Put water onto one watch glass, creating a puddle about the size of a quarter.
- 3. Put the unknown liquid onto the other watch glass, creating the same size puddle.
- 4. Note the time on a note pad.
- 5. Periodically compare the evaporation rate of the unknown liquid to that of the water. If the unknown liquid evaporates faster than the water does, it has a higher vapor pressure. If it evaporates slower than the water does, it has a lower vapor pressure. (Water has a vapor pressure of about 25 millimeters of Mercury at 68°F.)

This test gives you information on both the inhalation hazard and the fire hazard. If the vapor pressure is greater than that of water, the vapors can readily get into the air, making the liquid a potential inhalation hazard. The faster the product evaporates, the greater the hazard. If the product is flammable, a higher vapor pressure also means that more flammable vapors are being produced, increasing the fire hazard. Also, the higher the vapor pressure, the lower the flash point.

#### **Step 2 - Check Water Behavior**

- 1. Put a small amount of water into a test tube.
- 2. Put up to 5 drops of the unknown liquid into the test tube. (Adding a drop of potassium permanganate will help make the product visible.)
- 3. Gently shake the test tube to help mix the solution. Be careful not to spill anything.
- 4. Observe whether the product floats, sinks, or mixes with water.

This test gives you information about where the product will be if spilled in water. It also gives you limited information about the hazards associated with the product and how you might handle a release.

If the product floats on water, it is probably a hydrocarbon and is probably either flammable or combustible. Using water to fight a fire is likely to spread it. Consider using a dry chemical extinguisher or foam on a small fire. It may be best to let a large fire burn while protecting exposures instead. If the product spills into a waterway, you may need to construct an underflow dam to contain it.

If the product sinks, it is probably toxic, making respiratory protection a high priority. The product is likely to contain halogens (such as chlorine, bromine, iodine, or fluorine) and, as such, will most likely be non-flammable, but could be a strong oxidizer. Other potential sinkers include organic substances containing phosphorus or sulfur. If the product spills into a waterway, you may need to construct an overflow dam to contain it.

If the product mixes with water, it is water-soluble. A great many chemicals fall into this category, so it is difficult to make generalizations about what type of product it may be or what hazards are associated with it. In terms of mitigation, you may be able to dilute the product with water, thereby reducing its vapor pressure. A lower vapor pressure means that less vapor is getting into the air, thereby reducing any toxicity hazard and/or flammability hazard. Remember, however, that adding water increases the overall volume of product that must be contained and disposed. If the product spills into a waterway, you may need to construct a simple dam to contain it.

# Step 3 - Check pH

- 1. Wet a strip of pH paper, then place the colored portion of the pH paper into the liquid.
- 2. Remove the pH paper from your sample and read the pH by comparing the colors on the pH paper with the colors on the pH strip box. (Make sure you orient the colored part of the strip with the colored part of the box and the white part of the strip with the white part of the box. Otherwise, you will get an inaccurate reading.)

This test gives you information regarding the corrosivity of the product. A pH of 0, 1, or 2 indicates a strong acid, whereas a reading of 12, 13, or 14 indicates a strong caustic (also called base or alkali). Beware! Either extreme is very corrosive to human tissue. A pH of 7 is neutral, but a pH anywhere from 5 to 9 is considered safe in terms of corrosivity. (Motor oil normally has a pH of 5.)

## Step 4 - Check for Flammability

Steps 4 and 5 apply to all floaters and sinkers, as well as to swimmers with a pH anywhere from 4 to 9. It is not required for swimmers with a pH of 0 to 3 or 10 to 14.

- 1. Place a small amount of the liquid on a watch glass. (If possible, elevate the watch glass by putting it on a Bunsen burner stand. If you don't have some kind of platform upon which to place the watch glass, you can position it near the edge of your table.)
- 2. Light a match, then slowly bring the match toward the base of the Bunsen burner stand (or toward the edge of the table, several inches below the watch glass.)
- 3. Slowly move the match upward, moving it closer to the watch glass. If the vapors ignite, pull the match away and take note of where the match was when ignition occurred.
- 4. If the vapors haven't ignited yet, continue moving the match upward until it is above the liquid. If the vapors still haven't ignited, touch the flame to the liquid.

This test gives you information on flammability, flash point, and vapor density. If the vapors ignite, the liquid is flammable. If not, you need to do the next test to determine whether the product is combustible or noncombustible.

The vapors of any liquid are heavier than air; however, some are heavier than others. If the vapors ignited and flashed back to the liquid in the watch glass while your match was still well below the product, you have a very dangerous flammable liquid whose vapors can easily ignite and flash back to the source. It likely has a very low flash point as well. If the vapors did not ignite until you held the match just over the liquid, you still have a flammable liquid. However, due to a higher flash point, a narrower flammable range, a lower vapor pressure, and/or a lighter vapor density, the product does not ignite as easily.

If this flammable liquid floated on water during the Water Behavior Test (Step 2), you are probably dealing with a hydrocarbon. Flame color can help you narrow it down further. A clean orange flame is typical of saturated and unsaturated hydrocarbons. A dirty, sooty flame is indicative of aromatic hydrocarbons (benzene, toluene, xylene, styrene, or cumene).

If this flammable liquid is a sinker, it most likely contains phosphorus or sulfur. However, some alkyl halides are also flammable.

The most common flammable swimmers include alcohols and ketones. Other strong possibilities include the carbonyls (materials with a double bond between carbon and oxygen), such as aldehydes and esters.

Obviously, responders need flash or thermal protection from any of the flammable liquids. In addition, skin protection from vapor contact is usually needed for the flammable sinkers and the aromatic hydrocarbons because of the toxicity hazard.

Vapor suppression is usually done with aqueous film-forming foam (AFFF) for floaters, a water blanket for sinkers, or alcohol-type foam (ATF) for swimmers.

#### **Step 5 - Check for Combustibility**

If the product did not ignite in the previous test, check for combustibility.

- 1. Set up a small torch.
- 2. Take two Q-tips, dipping one into the unknown liquid.
- 3. With the torch blowing flame away from you, take a Q-tip in each hand and slowly bring them both toward the flame, keeping each Q-tip at the same distance from the flame. Keep bringing them toward the torch until they almost touch the flame. Observe which one ignites first.

If the Q-tip with the unknown liquid ignites first, the product is combustible. If not, the product is noncombustible.

In general, the guidelines that apply to flammable liquids also apply to combustible liquids. However, depending on other variables present on scene, you may have a little more latitude for thermal protection. In other words, you may have the option to focus more on the toxicity risks than you would with a flammable liquid.

# Simplified Field ID for Unknown Solids

Developed by Kevin Smith, Deputy Fire Marshal - Hazardous Materials Chino Valley Independent Fire District

You can often tell a lot about the type of product you are dealing with and the hazards associated with it through simple observation and by doing a few easy tests. The following information is a brief guide. It is not a substitute for more thorough testing or further research using available reference materials. However, it can give you a basis of information from which to make initial response decisions.

#### **Step 1 - Check Water Behavior**

- 1. Put a small amount of the unknown solid onto a watch glass.
- 2. Add a few drops of water.
- 3. Carefully observe the behavior for indications of water-reactivity.

(The Water Behavior Test is usually done by adding a small sample of the solid to water in a test tube. However, if a product is water-reactive, it can generate a strong enough reaction to break that test tube. By first checking for water-reactivity on a watch glass, you can minimize the risk of injury. If the product is not water-reactive or if the reaction is relatively mild, you can proceed with the following instructions. If it reacts strongly with water, you can limit your observations to what you see on the watch glass.)

- 4. Put a small amount of water into a test tube.
- 5. Add a few granules of the solid.
- 6. Wearing latex gloves, feel below the water line of the test tube for a change in temperature.
- 7. Observe whether or not the product dissolves in water and how completely it dissolves if it is soluble.

A product that is water-reactive presents a challenge under fire conditions. Small fires may be fought with dry chemical extinguishers (or Class D extinguishers in the case of combustible metals). However, in the event of a large fire, the best option may be to let the fire burn and protect exposures instead.

If spilled, a water-reactive material will obviously be a problem on rainy days. However, these materials will also react with moisture in the air on a humid day or with moisture on someone's skin or in someone's eyes. Don't overlook these less obvious sources of moisture.

If the product completely dissolves in water, it may be a salt. Many salts are toxic.

#### Step 2 - Check pH

- 1. Before discarding the contents of the test tube used in the previous step, wet a strip of pH paper, then place the colored portion of the pH paper into the liquid.
- 2. Remove the pH paper from your sample and read the pH by comparing the colors on the pH paper with the colors on the pH strip box. (Make sure you orient the colored part of the strip with the colored part of the box and the white part of the strip with the white part of the box. Otherwise, you will get an inaccurate reading.)

This test gives you information regarding the corrosivity of the product. A pH of 0, 1, or 2 indicates a strong acid, whereas a reading of 12, 13, or 14 indicates a strong caustic (also called base or alkali). Beware! Either extreme is very corrosive to human tissue. A pH of 7 is neutral, but a pH anywhere from 5 to 9 is considered safe in terms of corrosivity.

#### **Step 3 - Check for Explosivity**

- 1. Place a small amount of the unknown solid onto a watch glass.
- 2. Heat the end of a thin metal wire. (A coat hanger works well. To protect from burning your fingers, you should insert the opposite end of the wire into a cork or other nonconductive object that you can use as a handle.)
- 3. Carefully touch the heated end of the wire against part of the solid sample.

If the sample "pops," it is probably explosive. If not, there is still a possibility it could be flammable or combustible. Go on to Step 4.

#### **Step 4 - Check for Flammability**

If the product did not "pop" in the previous test, check for flammability.

- 1. Place a small amount of the solid onto a watch glass.
- 2. Light a match, then slowly bring the match toward the watch glass. Move it just over the top of the sample.
- 3. If the sample hasn't ignited yet, touch the flame to the sample.

If the sample ignites, you have a flammable solid. If the flame goes out when you touch it to the sample, the product is not flammable but may still be combustible. Go on to Step 5.

## Step 5 - Check for Combustibility

If the product did not ignite in the previous test, check for combustibility.

- 1. Set up a small torch.
- 2. Place a small amount of your sample on one lab spatula and an equal amount of sugar on another.
- 3. With the torch blowing flame away from you, take a lab spatula in each hand and slowly bring them both toward the flame, keeping each spatula at the same distance from the flame. Keep bringing them toward the torch until they almost touch the flame. (Do not get the samples into the flame.) Observe the reactions.
- 4. Once the product ignites or the sugar melts, stop. There is no need to test further.

Sugar melts at approximately 200°F. Therefore, if your unknown sample ignites before the sugar melts, the sample is combustible and has flash point *less than* 200°F. If the sugar melts before the sample ignites, the product has a flash point *greater than* 200°F. If the sample does not ignite at all during this test, it indicates that either the product is noncombustible or it must be heated further for ignition to occur.

Some products will melt or decompose rather than ignite. Solids that decompose when heated can be either reducing agents or oxidizing agents. Many are organic compounds.

# **Water and Fire Behavior Overview**

The following chart provides an overview of how various types of materials behave during the water behavior and fire behavior tests in the Haz Cat or 5-Step field identification tests. Keep in mind that these are general guidelines only, that there are sometimes variations within a particular group, and that there may be exceptions in each category. **Do not rely solely on this chart.** 

Materials	Water	Fire Behavior	Flame Color	Smoke
	Behavior			Characteristics
Hydrocarbons (H & C)				
Alkanes	Floats	Varies. May ignite with match above or below. May need to be heated.	Depends	Depends
Alkenes	Floats (reacts with KMnO <sub>4</sub> )	Varies. May ignite with match above or below.	Yellow	Yellow
Alkynes	Floats (reacts with KMnO <sub>4</sub> )	Ignites with match above.	Blue/Yellow	
Aromatics	Floats	Ignites with match above.		Black and sooty
Isomers		Varies. May ignite with match above or below. May need to be heated.	Depends	Depends
Part 1 HCDs (carbonyls)				
Ketones	Swims	Ignites with match above.	Blue/Clear	Little or none
Aldehydes	Swims	Ignites with match above. May also ignite with match below. May need to be heated.	Yellow/Orange	Black and sooty
Organic Acids	Swims	Ignites with match above.	Yellow/Orange	Black and sooty
Esters	Swims	Varies. May ignite with match below. May need to be heated.	Yellow	Black and sooty
Part 1 HCDs (others)				
Alcohols	Swims	Ignites with match above.	Blue/Clear	Little or none
Glycols	Swims	Ignites when heated.	Orange	Black and sooty
Ethers	Swims	Ignites with match above.	Blue/Clear	Little or none
Glycerols	Swims	Ignites when heated.	Orange	Black and sooty
Organic Peroxides	Swims	Ignites with match above.	Blue/Yellow	Little
Part 2 HCDs (H, C, N)				
Nitros	Swims	Ignites with match above.	Blue/Clear	Little
Amines	Swims	Ignites with match above.		
Amides	Swims	Varies. May ignite with match above or below.		
Carbamates	Swims	Varies. May ignite with match above or below.		
Nitriles	Swims	Ignites with match above.	Blue/Clear	Little
Part 2 HCDs (others)				
Thiols (Mercaptans)	Sinks	Varies. May ignite with match above or below. May need to be heated.	Orange	Black and sooty
Alkyl Halides	Sinks	Won't burn.		
Organophosphates	Swims	May or may not burn.		Black and sooty
High-Tech Compounds Inorganic Acids	Depends Swims (reacts with KMnO <sub>4</sub> )	Won't burn.		

# **Chemical Name and Formula Recognition**

Developed by Kevin Smith, Deputy Fire Marshal - Hazardous Materials Chino Valley Independent Fire District

# Ordered Alphabetically by Suffix

Prefix	Suffix	Family	Formula Contains	Hazards/Characteristics
	??	Organo-phosphate	Р	Toxic. (Pesticide)
	acid	Organic acid	C00H	Corrosive.
	aldehyde	Aldehyde	СНО	Flammable, toxic, soluble. Avoid skin contact.
	amine	Amine	NH <sub>2</sub>	Toxic, foul odor. May cause liver/kidney damage.
	ane	Alkane	H&C only	Flammable.
iso	ane	Alkane w/ branched chain	H&C only	Lower flash point and higher vapor pressure than regular alkanes.
	ate	Ester (no metal)	COO	Flammable. Liver and kidney damage.
	ate	Oxysalt (if metal involved)		Oxidizer. "Ate" indicates normal state.
per	ate	Oxysalt (if metal involved)		Strong oxidizer. "Per" indicates extra oxygen.
	carbamate	Carbamate	NH <sub>2</sub> COO	Toxic. (Pesticide)
	cyanide	Cyanide salt (has metal)	CN	Toxic. Avoid acids.
	ene	Alkene	H&C only	Flammable. Violent polymerization possible.
iso	ene	Alkene w/ branched chain	H&C only	Lower flash point and higher vapor pressure than regular alkenes.
	ene	Aromatic (based on benzene ring)	H&C only	Toxic and combustible.
	ether	Ether	0	Wide flammable range, BLEVE, toxic, unstable if old.
	glycerine	Glycerol	(OH) <sub>3</sub>	Combustible.
	glycol	Glycol	(OH) <sub>2</sub>	Combustible, toxic, polar, odorless.
	hydroxide	Hydroxide salt	OH	Caustic.
	ide	Alkyl halide (no metal)	F, CL, BR, I	Toxic, nonsoluble. Some burn.
	ide	Binary salt (has metal)		May be toxic, corrosive.
	ite	Oxysalt (if metal involved)		Oxidizer. One oxygen below normal state.
hypo	ite	Oxysalt (if metal involved)		Oxidizer. Two oxygens below normal state.
	ol	Alcohol	(OH)	Wide flammable range, toxic, polar.
	one	Ketone	CO	Flammable, toxic.
	onitrile	Nitrile	CN	Toxic. Contains cyanide.
	oxide	Oxide salt (has metal)	0	In water, makes caustic solution and heat.  Not an oxidizer.
	peroxide	Organic peroxide (no metal)	0-0	Unstable, explosive, oxidizer.
	peroxide	Peroxide salt (has metal)	O <sub>2</sub>	Oxidizer.
	sulfide	Binary salt (has metal)	S	In acid, makes hydrogen sulfide gas.
	thiol	Thiol	SH	Flammable, toxic, irritants, skunk-like odors.
	yne	Alkyne	H&C only	Flammable. Explosive. May be shock-sensitive.
iso	yne	Alkyne w/ branched chain	H&C only	Lower flash point and higher vapor pressure than regular alkyne.
nitro		Nitro	NO <sub>2</sub>	Explosive. Possibly shock-sensitive. Fire risk. Toxic.

# **Spill Estimation Chart**

Developed by Kevin Smith, Deputy Fire Marshal - Hazardous Materials Chino Valley Independent Fire District

This table was constructed based on assumptions used by FEMA and the U.S. EPA for emergency planning purposes. The data and formulations are specifically from Appendix G, "Equations Used for the Estimation of Vulnerable Zones," Technical Guidance for Hazard Analysis (1987), and from the Unit Equivalency Table, page A-4, of the *Handbook of Chemical Hazard Analysis Procedures*.

Radius	Diameter	Area	Gallons	Weight*
(feet)	(feet)	(sq. ft.)		(pounds)
1	2	3	0.8	6.5
2	4	13	3.1	25.9
3	6	28	7.0	58.2
4	8	50	12.4	103.5
5	10	79	19.4	161.7
6	12	113	28	233
7	14	154	38	317
8	16	201	50	414
9	18	254	63	524
10	20	314	78	647
11	22	380	94	783
12	24	452	112	931
13	26	531	131	1093
14	28	616	152	1268
15	30	707	174	1455
16	32	804	199	1656
17	34	908	224	1869
18	36	1018	251	2095
19	38	1134	280	2335
20	40	1257	310	2587

Radius	Diameter	Area	Gallons	Weight*
(feet)	(feet)	(sq. ft.)		(pounds)
21	42	1385	342	2852
22	44	1521	375	3130
23	46	1662	410	3421
24	48	1810	447	3725
25	50	1963	485	4042
26	52	2124	524	4372
27	54	2290	565	4715
28	56	2463	608	5070
29	58	2642	652	5439
30	60	2827	698	5821
31	62	3019	745	6215
32	64	3217	794	6623
33	66	3421	844	7043
34	68	3632	896	7476
35	70	3848	950	7923
36	72	4072	1005	8382
37	74	4301	1062	8854
38	76	4536	1120	9339
39	78	4778	1179	9837
40	80	5027	1241	10,348

# **Using the Information with Circular Spills**

This chart assumes that the spill is a circular one and that the spill is 0.033 feet (1 centimeter) deep. (Note: These same calculations can be used for spills contained within circular dikes.)

- 1. Determine either the radius or the diameter.
- 2. Read the "Gallons" and "Weight" columns in that row.
- 3. If the spill depth is either more or less than one centimeter, multiply or divide the numbers as appropriate. (If measuring in inches, convert inches to centimeters by multiplying by 2.54.)

#### Using the Information with Rectangular Spills

If the spill is rectangular rather than circular, you must first calculate the area of the spill to determine gallons and pounds. (Note: These same calculations can be used for spills contained within rectangular dikes.)

- 1. Figure the area by multiplying length times width.
- 2. Find the closest match in the "Area" column.
- 3. Read the "Gallons" and "Weight" columns in that row.
- If the spill depth is either more or less than one centimeter, multiply or divide the numbers as appropriate. (If measuring in inches, convert inches to centimeters by multiplying by 2.54.)

#### **Conversion Factors**

1 cubic foot = 7.48 gallons

1 cubic foot = 30.30 square feet at 1 cm deep

1 gallon spill = 4.05 square feet at 1 cm deep

1 gallon of water = 8.34 pounds

1 inch = 2.54 centimeters

Diameter = Radius x 2

Area = Pi x  $R^2$  (3.14 x  $R^2$ )

<sup>\*</sup> Weight assumes a specific gravity of 1. For true weight, multiply the weight shown by the specific gravity of the product. (Specific gravity data is available on MSDSs and in various reference sources.

# **Your Instructors**

#### **Kevin Smith**

Kevin Smith serves as the Deputy Fire Marshal—Hazmat for the Chino Valley Independent Fire District. Kevin oversees the application of the Uniform Fire Code to hazardous materials occupancies in the 92-square-mile Chino Valley area and provides his expertise in hazardous materials emergencies, serving primarily in the Technical Reference role.

Kevin has 14 years' hazardous materials experience in the fire service. He is also a Hazardous Materials Instructor certified by the California Specialized Training Institute, one of a handful certified to teach the Chemistry modules for the Hazmat Tech/Spec series. He was one of the first federally-certified CAMEO instructors and currently teaches Hazmat Emergency Response and Hazmat Emergency Planning courses for the University of California Extension Program.

Kevin earned a Certificate in Hazardous Materials Management from the University at Irvine and holds a Master of Public Administration Degree from California State University at Fullerton. Kevin is also a Registered Environmental Assessor I with the State of California.

#### Jill Meryl Levy

Jill Meryl Levy owns her own business—Firebelle Productions. She is an author and publisher, with two full-length books to her credit. In 1996, she wrote and published her first book, *The First Responder's Pocket Guide to Hazardous Materials Emergency Response*, a field guide designed to help firefighters and other emergency responders manage a hazardous materials incident until a trained hazmat team arrives. She released a greatly expanded second edition in September 2000. In 1998, Jill released *Take Command of Your Writing*, a comprehensive guide to more effective writing geared specifically for emergency services personnel. Jill also produces brochures, booklets, and newsletters for fire departments and industry.

Jill has worked in the field of safety education since 1981 when she was hired by the City of Santa Clara Fire Department (CA). Later, during her employment at Hewlett-Packard Company in Cupertino (CA), Jill began producing brochures, booklets, and newsletters as a means to communicate safety information to a large employee population. The publications became so popular that she was soon producing brochures and booklets on a corporate-wide basis. Her last project before leaving the company was a 64-page employee handbook on health and safety responsibilities. She printed 56,000 copies for distribution in the United States, England, Scotland, Singapore, and Malaysia.

Jill first got involved with hazardous materials while working with the Governor's Office of Emergency Services California Specialized Training Institute (CSTI) on the 1994 and 1995 revisions of its *Hazardous Materials Technician/Specialist* curriculum. In 1995 she became a CSTI-certified hazardous materials specialist and a first responder outreach instructor. Jill has also assisted the California State Fire Marshal's Office with curriculum revision projects.

Jill has been a volunteer firefighter for the Santa Clara County Fire Department (CA) since 1980. In her spare time, Jill helps build homes with Habitat for Humanity.